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# The key feature of instability of small non-IPR closed-shell fullerenes: three isomers of $C_{40}$

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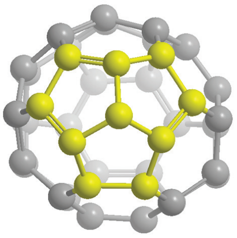
**The molecular structures of non-IPR $C_{40}$ fullerene isomers 31 ($C_s$), 38 ($D_2$) and 39 ($D_{5d}$) were studied using a semiempirical approach developed earlier for higher fullerenes. Quantum-chemical calculations (DFT) showed that they have closed shells. The distributions of single, double and delocalized π bonds in the test isomer molecules and their molecular formulas are presented for the first time.**



*Keywords*: small fullerene, bonds distribution, substructures, radical, strain, fused pentagons.

Small $C_n$ fullerenes ($n < 60$) are highly unstable due to a large strain energy; all of them violate the isolated pentagon rule (IPR).[1,2] Consequently, considering an experimental advance in the preparation of such fullerenes as derivatives,[3–7] the purpose of this theoretical study was to test the approach developed earlier for higher fullerenes[8,9] with small fullerenes in order to estimate the possibility of their production.

There are 40 non-IPR isomers of $C_{40}$ fullerene.[10] In contrast to the most stable $C_{60}$ and $C_{70}$ fullerenes and other IPR higher fullerenes, the structures and stabilities of small fullerenes were significantly less studied. An isomer with the lowest total energy and large HOMO–LUMO gap is 38 ($D_2$) cage with the smallest possible adjacency count (10) followed by isomer 39 ($D_{5d}$).[11–17] The presence of fused pentagons leads to structural distortions and enhanced local strains of the cage.[13,15,18] It was theoretically assumed that highly unstable open-shell isomer 40 ($T_d$) of $C_{40}$ fullerene can form a stable carbon–hydrogen cluster molecule $C_{40}H_4$ and carbon–halogen cluster molecules $C_{40}X_4$ (X = F, Cl, Br, I).[19,20] Therefore, in this work, we used the previously developed semiempirical approach to higher fullerenes[8,9] for studying the molecular structures of non-IPR $C_{40}$ fullerene isomers 31 ($C_s$), 38 ($D_2$), and 39 ($D_{5d}$), which are the most energetically favorable isomers,[13–17] in order to examine their instability and the possibility of their stabilization and production of various derivatives.

This approach provides a complete structural formula of fullerene with the distribution of single bonds, double bonds and π-delocalized bonds prior to quantum-chemical calculations. Using small $C_{40}$ fullerene as an example, we examined the applicability of this approach to similar small fullerenes. The molecular structures of the test $C_{40}$ fullerene isomers were fully optimized using the DFT B3LYP functional with 6-31G and 6-31G(d) basis sets in the GAUSSIAN 03 program.[21] A good agreement was obtained between the results of calculations performed for these basis sets. The quantum-chemical calculations for some isomers, which were treated like molecules with open-shell electronic structures, were carried out in configurations with high multiplicities using the unrestricted Kohn–Sham methodology.

The $C_{40}$ isomers 31 ($C_s$), 38 ($D_2$), and 39 ($D_{5d}$) are characterized by a closed shell without radical centers. The isomer 31 ($C_s$) molecule consists of three fragments of three, four and five adjacent pentagons and two *s*-indacene substructures (a hexagon with delocalized π bonds) [Figure 1(*a*)]. The isomer 38 ($D_2$) has two equivalent chains of six pentagons and two delocalized hexagons on each pole of the molecule [Figure 1(*b*)]. The generally most favored isomer 39 ($D_{5d}$) has a geodesic form with an equatorial belt of ten pentagons and two corannulene substructures (pentagon surrounded by five hexagons, like in fullerene $C_{60}$) on both poles [Figure 1(*c*)].

The presence of double bonds in adjacent pentagons, which contradicts the postulated single bonds in pentagon,[8,9] should also be noted. However, this is a common situation for non-IPR fullerenes.[22,23]

Quantum-chemical calculations showed that 38 ($D_2$) and 39 ($D_{5d}$) are the most stable isomers with a large HOMO-LUMO gap (Table 1); this is consistent with previously published data.[13–17] These isomers together with isomer 31 ($C_s$), as expected, have closed shells.

To determine structural parameters responsible for the instability of the non-IPR $C_{40}$ isomers, it is reasonable to compare their structural parameters with those of stable IPR

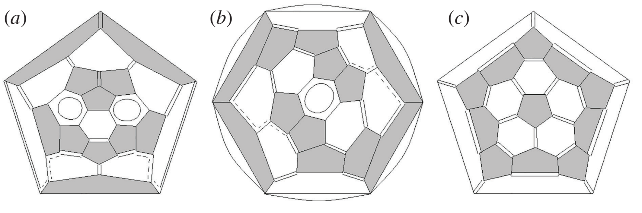


**Figure 1** Schlegel diagram of closed shell $C_{40}$ fullerene isomers (*a*) 31 ($C_s$), (*b*) 38 ($D_2$), and (*c*) 39 ($D_{5d}$). Single and double bonds are depicted by one and two lines, respectively, and delocalized π bonds are designated by a circle or dashed lines; all pentagons are in grey.

**Table 1** Relative energies $\Delta E$ (kcal mol$^{-1}$) and HOMO–LUMO gaps (eV) of $C_{40}$ fullerene isomers 31 ($C_s$), 38 ($D_2$), and 39 ($D_{5d}$).

| Isomer[a] | $E$ |  | HOMO–LUMO |  |
|---|---|---|---|---|
|  | 6-31G | 6-31G* | 6-31G | 6-31G* |
| 31 ($C_s$) singlet, M = 1 | 17.75 | 16.06 | 1.67 | 1.65 |
| triplet, M = 3 | 30.04 | 26.59 | 0.74 | 0.84 |
| 38 ($D_2$) singlet, M = 1 | 0.00 | 0.00 | 2.08 | 2.00 |
| triplet, M = 3 | 18.54 | 16.32 | 0.48 | 0.59 |
| 39 ($D_{5d}$) singlet, M = 1 | 10.98 | 10.47 | 2.24 | 2.15 |
| triplet $C_{2h}$, M = 3 | 35.63 | 32.77 | 0.17 | 0.28 |

[a] M is the multiplicity of the corresponding electronic configuration.

isomers [*e.g.*, experimentally studied most stable $C_{60}$ ($I_h$) and $C_{70}$ ($D_{5h}$) fullerenes[24,25]]. The preliminary bond distributions found according to the developed approach were confirmed by DFT calculations: calculated bond lengths corresponded to single, double and delocalized π bonds plotted on Schlegel diagrams, and they were in agreement with the well-known experimental values for $C_{60}$ and $C_{70}$ fullerenes[24,25] (Tables 2 and S1).

In higher fullerenes,[8,9] the high distortion of a fullerene cage, *i.e.*, the high nonplanarity of hexagons and pentagons, reflects a local strain of a fullerene molecule, which directly relates to its thermodynamic instability. A molecule of the most stable $C_{60}$ fullerene consists of planar hexagons and pentagons,[24] but some distortions of hexagons and pentagons appear in $C_{70}$ fullerene to reach maximum values in hexagons with delocalized π bond.[26] These distortions in the molecules of higher fullerenes may compensate the π-delocalization of hexagons imbedded in a sphere-like fullerene cage. In fullerenes with substantially smaller sphere sizes, the influence of local strains on the molecular stability obviously plays a much larger role. An analysis of the molecular geometries of the $C_{40}$ isomers showed that all hexagons and pentagons are not flat (Figure 2, Table S2).

However, the presence of pentalene fragments or other fragments with fused pentagons, which can introduce significant strains in the molecules, is more important for small non-IPR fullerenes. The non-fullerene analogs of the pentalene fragments retain their flat structure due to their sp$^2$-hybridized atoms, including cases where metal cations are coordinated with each pentagon of pentalene fragments.[27] This is true for a molecule with a linear chain of four fused pentagons.[28]

**Table 2** Bond lengths (Å) in $C_{60}$ ($I_h$) and $C_{70}$ ($D_{5h}$) fullerenes and $C_{40}$ isomers 31 ($C_s$), 38 ($D_2$), and 39 ($D_{5d}$).

| Isomer | single |  | double |  | delocalized |  |
|---|---|---|---|---|---|---|
|  | min | max | min | max | min | max |
| $C_{60}$ ($I_h$)[24] | 1.459 |  | 1.397 |  | - |  |
| $C_{70}$ ($D_{5h}$)[25] | 1.454 | 1.477 | 1.390 | 1.399 | 1.424 | 1.439 |
| $C_{40}$ 31 ($C_s$) singlet | 1.443 | 1.509 | 1.370 | 1.402 | 1.414 | 1.436 |
| $C_{40}$ 38 ($D_2$) singlet | 1.450 | 1.499 | 1.369 | 1.397 | 1.409 | 1.435 |
| $C_{40}$ 39 ($D_{5d}$) singlet | 1.455 | 1.489 | 1.371 | 1.409 | - | - |

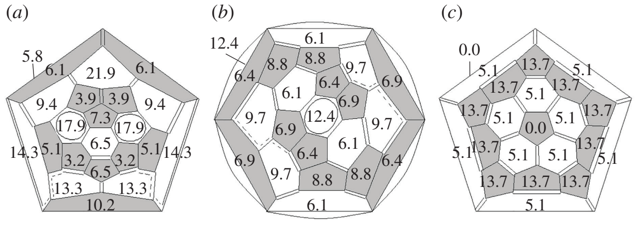


**Figure 2** Schlegel diagrams with maximal dihedral angles (degree) in cycles in $C_{40}$ fullerene isomers (*a*) 31 ($C_s$), (*b*) 38 ($D_2$), and (*c*) 39 ($D_{5d}$).

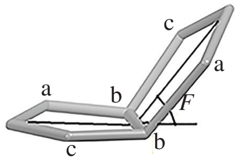


**Figure 3** Folding angle $F$ between pentalene fragments.

Therefore, we can use the folding angle $F$ as a parameter of strains in the molecules (Figure 3); $F = 0°$ for flat molecules. In a fullerene molecule, the folding of an initially flat pentalene structure determined by a sphere-like molecular geometry leads to significant local strains. The hypothetical molecules of pristine $C_{40}$ isomers 31 ($C_s$), 38 ($D_2$), and 39 ($D_{5d}$) show folding angles of 44.4–54.4° (Table S3); therefore, they experience high overstrain and cannot exist. To evaluate the molecular strain or curvature of a fullerene shell, so-called pyramidalization angle proposed by Haddon ($\theta_p = \theta_{\sigma\pi} - 90°$; for graphite, $\theta_p = 0$) is used.[29] However, this method is more difficult to implement, and also it can lead to erroneous conclusions because an increase in the size of a fullerene molecule with a constant number of pentagons causes a decrease in molecular strains. The pyramidalization angle is 11.60° in the most strained IPR $C_{60}$ fullerene, while it ranges from 8.90 to 12.00° in $C_{70}$ fullerene.[29,30]

Thus, the quantum-chemical calculations (DFT) demonstrated that isomers 31 ($C_s$), 38 ($D_2$), and 39 ($D_{5d}$) have closed electronic shells. The main factor of their instability is the high folding angle between the pentagons of pentalene fragments, which is the reason for local overstrains in the molecules. Thus, our approach previously developed for higher fullerenes is also applicable to smaller fullerenes.

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*Online Supplementary Materials*

Supplementary data associated with this article (calculated bonds lengths of singlet configurations; maximal dihedral angles in hexagons and pentagons; dihedral angles and folding angles of pentagonal fragments in molecules of isomers 31 ($C_s$), 38 ($D_2$) and 39 ($D_{5d}$) of fullerene $C_{40}$) can be found in the online version at doi: 10.1016/j.mencom.2020.11.012.

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